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PLASMA-MODIFIED THERMAL CARBON BLACK AS A PACKING MATERIAL FOR GAS CHROMATOGRAPHY

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SUMMARY

The chromatographic properties of thermal carbon black (TCB) TG-10 could be improved by treating it with a high-frequency plasma, in the presence of benzene vapour. In comparison with the untreated TCB, chromatographic peaks are more symmetrical and retention volumes are lower. The data obtained show that the surface of TCB after modification becomes more uniform and non-specific, and the properties of modified TCB approach those of graphitized carbon black.

TCB modified in this manner is good sorbent for selective separation of structural and geòmetrical isomers.

INTRODUCTION

The use of carbon black as a sorbent for gas chromatography (GC) is of interest from both theoretical and analytical points of view, since the adsorption process on carbon black with a chemically uniform surface is based only on non-specific interactions. Unfortunately, with a few exceptions such as "Sterling" graphitized carbon black, the surface of industrial carbon black possesses also oxygen-containing adsorption centres, which impart a specific character to the sorbent–sorbate interactions and as a rule result in a deterioration of the properties of carbon black as a packing for GC purposes.

Our earlier work[1,2] demonstrated the possibility of modifying supports for gas–liquid chromatography including thermal carbon black[3] by polymer coating in plasma. This paper describes an attempt to improve the chemical uniformity of carbon black having a partially oxidized surface by treatment with benzene vapour in a high-frequency, low-temperature plasma.

EXPERIMENTAL

The experiments were carried out using an industrial thermal carbon black Type TG-10 of specific surface area 8 m^2/g. Two sieve fractions, *i.e.*, from 0.14 to

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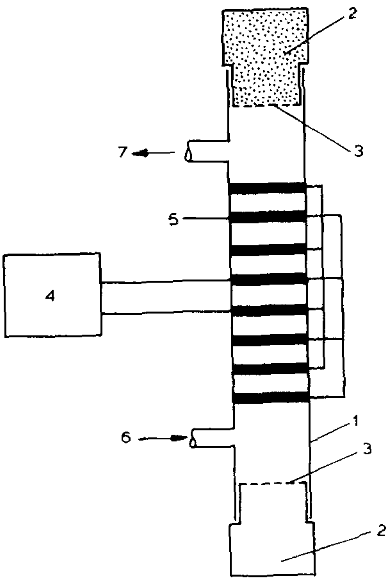

Fig. 1. Apparatus for treating in high-frequency plasma. 1 = Reactor; 2 = containers; 3 = sieve plates; 4 = high-frequency generator; 5 = ring electrodes; 6 = monomer and argon inlet; 7 = rotary vacuum pump.

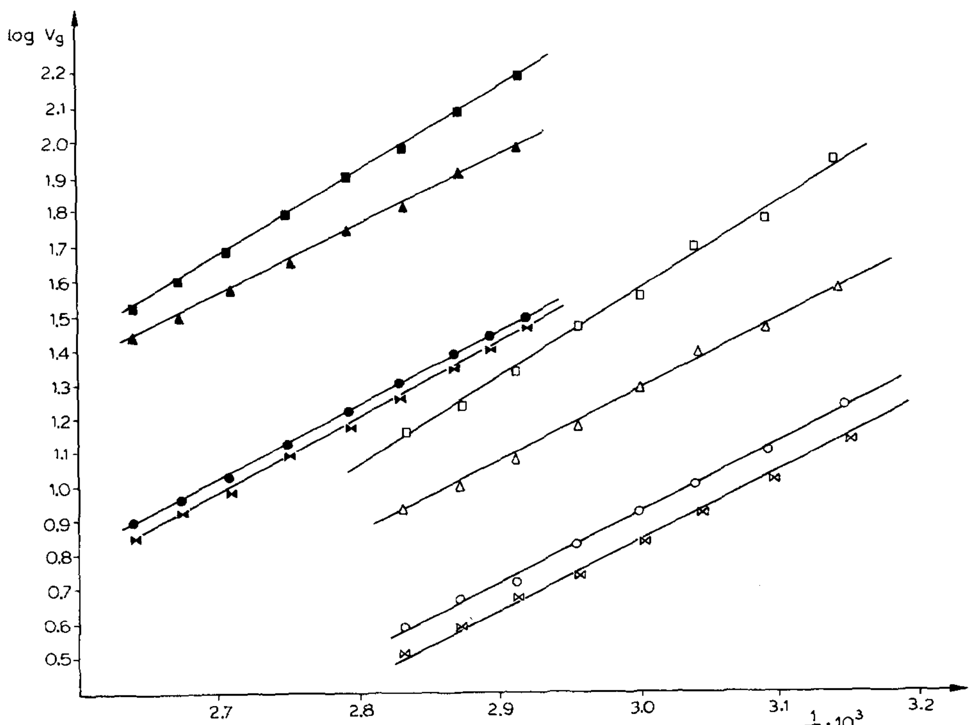

Fig. 2. Plot of the logarithm of the retention volumes *vs.* reciprocal absolute temperature: (▲) $-C_6H_6$; (●) $-C_5H_{12}$; (⧓) $-(C_2H_5)_2O$; (■) $-C_6H_{14}$ on carbon black TG-10 and (△) $-C_6H_6$; (○) $-C_5H_{12}$; (⋈) $-(C_2H_5)_2O$; (□) $-C_6H_{14}$ on TG-10 modified with benzene in plasma.

TABLE I

DIFFERENTIAL MOLAR INTERNAL ENERGIES AT ZERO SURFACE COATING $-\Delta U_1$ (kJ/mol)

Compound	*TG-10*	*Benzene-modified TG-10*	*GTCB Sterling MT*
n-Pentane	41.7	38.3	33.5
n-Hexane	47.5	45.9	38.4
Benzene	40.4	38.3	36.2
Diethyl ether	38.3	35.7	31.6

0.16 mm and from 0.25 to 0.50 mm, respectively, were chosen upon granulation. A preliminary treatment in argon plasma was carried out in order to purify the carbon black surface. Then, treatment with benzene vapour was performed. Attempts to use naphthalene vapour were not successful. The reactor of the apparatus (Fig. 1) was connected to a 40-W, 13.5-MHz high frequency generator. A residual pressure of 1 Torr was maintained. The treatment time was 2 sec.

Chromatographic measurements were made using a Tzvet 110 chromatograph with a flame ionization detector and 1-m column. *n*-Pentane, diethyl ether, *n*-hexane and benzene were used as adsorbates. These molecules possess similar geometries and sizes but different structures and properties, which permits some conclusions to be drawn about the surface chemistry on the basis of the retention volumes and of the data on the internal energy at zero surface coating, $-U_1$.

RESULTS AND DISCUSSION

As a result of the benzene vapour treatment of thermal carbon black in a low

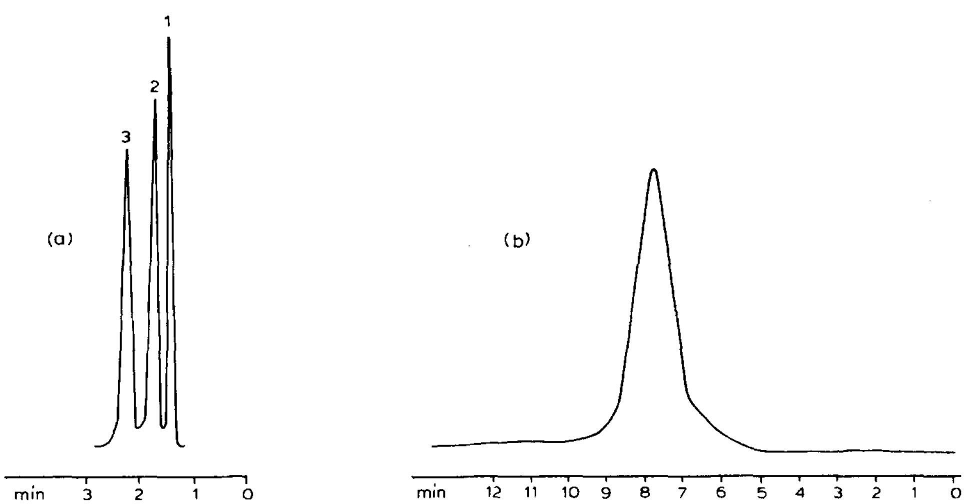

Fig. 3. Chromatograms: (a) mixture of (1) 2-methylbutene-2; (2) 3-methylbutene-1; (3) 2-methylbutene-1; (b) 3-methylpentene-2. Column with TG-10, 100 × 0.3 cm, particle diameter 0.3–0.5 mm, temperature 323°K.

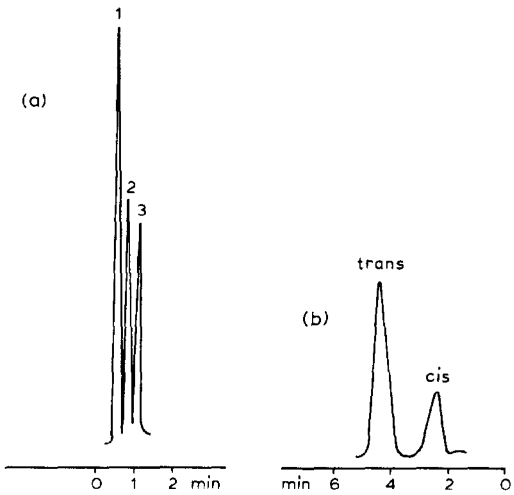

Fig. 4. Chromatograms: (a) mixture of (1) 2-methylbutene-2; (2) 3-methylbutene-1; (3) 2-methylbutene-1; (b) 3-methylpentene-2. Column with TG-10, modified in argon plasma with benzene, 100 × 0.3 cm, particle size 0.3–0.5 mm, temperature 323°K.

frequency plasma, both the retention volumes (Fig. 2) and the adsorption heats (Table I) for all the four adsorbates investigated decreased. Concerning the adsorption heats, this modified carbon black resembled the graphitized thermal carbon black of type Sterling MT[4]. This is due to a pyrographite coating formed under the conditions of the low frequency plasma which is similar to that obtained thermally[5].

From the relationships log $V_g = f(1/T)$ (Fig. 2) for the untreated and modified carbon black, respectively, it is evident that the retention volumes and the adsorption heats of benzene are lower than those of *n*-hexane irrespective of the significantly lower boiling point of the latter. The adsorption behaviour of these adsorbates on graphitized thermal carbon black of the type Sterling MT was similar. A comparison between the values for diethyl ether and pentane (Table I) shows the surface uniformity of benzene-modified thermal carbon black.

A considerable improvement in the GC properties of the sorbent is achieved. The decrease in adsorption parameters due to the specific reactions leads to a decrease in the retention volumes and times, respectively, as well as to an improvement in peak symmetry. It is known that Graphon carbon black, which possesses approximately 1% active centres, gives asymmetric peaks, while Sterling carbon black, which possesses approximately 0.1% surface active centres, behaves as a sorbent of uniform surface and gives symmetric peaks[6]. The argon plasma treatment of the sorbent results in a considerable improvement in its properties as a GC packing.

For example, when a column of 3 mm I.D. containing unmodified TG-10, *i.e.*, the fraction between 0.3 and 0.5 mm, is used at a temperature of 323°K a mixture of isomeric methylbutenes is separated in 2 min 21 sec (Fig. 3a), but a mixture of *cis*- and *trans*-isomers of 3-methylpentene-2 is not resolved after about 8 min at 323°K (Fig. 3b). On benzene vapour-modified carbon black TG-10 the first mixture is separated after about 1 min 30 sec (Fig. 4a) under the same chromatographic conditions, and the second mixture is separated in about 5 min at the same temperature (323°K).

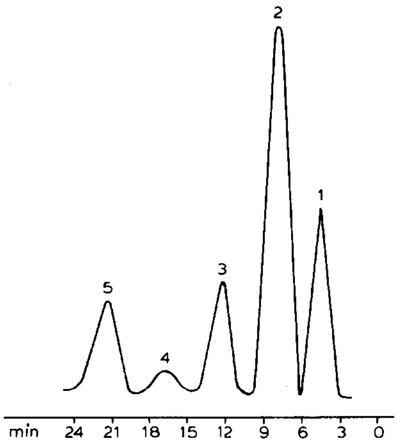

Fig. 5. Separation of perhydroanthracene isomers on TG-10 modified with benzene in plasma. Column 100 × 0.3 cm, 423°K, particle diameter 0.14–0.16 mm. Peaks: 1 = *cis-syn-cis*; 2 = *cis-syn-trans*; 3 = *cis-anti-cis*; 4 = *trans-anti-trans*; 5 = *trans-syn-trans*.

The advantages of the benzene-modified carbon black are also shown in the separation of stereoisomers of perhydroanthracene. Whereas this separation could not be achieved on a column of unmodified carbon black, a satisfactory separation on the modified sorbent, *i.e.* the fraction between 0.14 and 0.16 mm, is obtained in about 24 min at 423°K using a column of 1 mm I.D. (Fig. 5).

The symmetry of the chromatographic peaks obtained with the modified sorbent was improved in all the cases investigated.

In conclusion, the modification of thermal carbon black using benzene vapour in plasma leads to an improvement in its analytical GC properties, which become similar to those of graphitized carbon black of the Sterling type, thus permitting the separation of complex mixtures of organic compounds.

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